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(19) (CA) **CANADIAN PATENT** (12)

(54) DISAZO COMPOUNDS, PROCESS FOR THEIR  
MANUFACTURE AND THEIR USE

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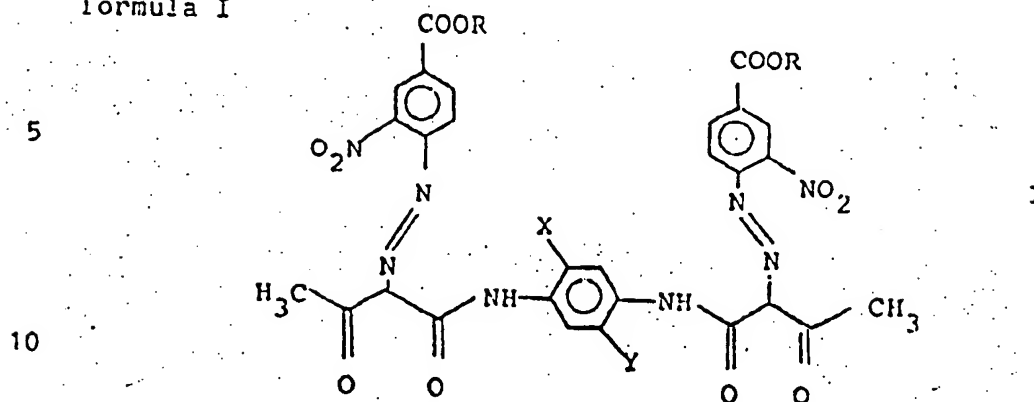
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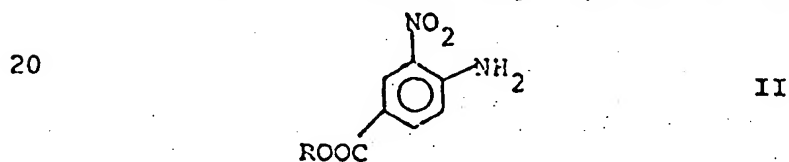
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Subject of the invention are disazo compounds of the formula I

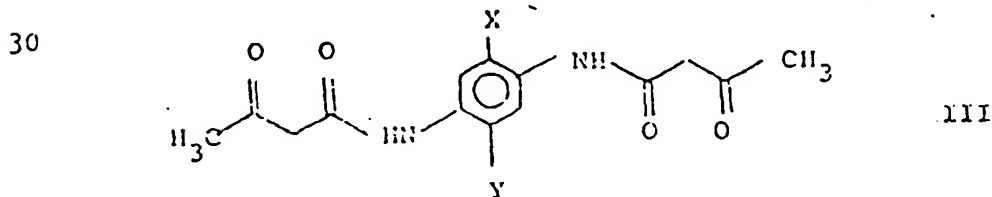


in which R is alkyl with from 1 to 4 carbon atoms,  
X and Y are hydrogen, chlorine, bromine, methyl, ethyl,  
methoxy or ethoxy.

15 The invention further relates to a process for the  
manufacture of the above-mentioned disazo compounds,  
which comprises diazotizing compounds of the formula II



in which R has the meaning mentioned for formula I,  
and coupling two molar equivalents of the diazonium  
25 compound obtained, or of the mixture of two or more  
diazonium compounds from compounds of formula II with  
one molar equivalent of a compound, or a mixture of  
two or more compounds of the formula III



35 in which X and Y are as defined for formula I above.



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Another subject of the invention is the use of the disazo compounds of the invention as colorants, especially as pigments.

- 5 Suitable amines of the formula II are, for example:
- 3-Nitro-4-aminobenzoic acid methyl ester
  - 3-Nitro-4-aminobenzoic acid ethyl ester
  - 3-Nitro-4-aminobenzoic acid-n-propyl ester
  - 3-Nitro-4-aminobenzoic acid-isopropyl ester
  - 10 3-Nitro-4-aminobenzoic acid-n-butyl ester
  - 3-Nitro-4-aminobenzoic acid-isobutyl ester
  - 3-Nitro-4-aminobenzoic acid-1'-methyl-propyl ester.

- 15 The amine of the formula II may be diazotized for example with alkali metal nitrites or lower alkyl nitrites with sufficiently strong acids, especially a mineral acid, but also with nitrosylsulfuric acid. In this process step as well as in the subsequent coupling it may be advantageous to add surface-active
- 20 agents, such as non-ionic, anionic or cationic dispersing agents. The diazotization is suitably carried out at  $-10$  to  $+30^{\circ}\text{C}$ , and the coupling is effected at  $0$  to  $40^{\circ}\text{C}$ .

- 25 As coupling components there may be used, for example:
- 1,4-Bisacetoacetylaminobenzene,
  - 1,4-Bisacetoacetylamino-2-chlorobenzene,
  - 1,4-Bisacetoacetylamino-2,5-dichlorobenzene,
  - 1,4-Bisacetoacetylamino-2-methylbenzene,
  - 30 1,4-Bisacetoacetylamino-2,5-dimethylbenzene,
  - 1,4-Bisacetoacetylamino-2-methoxybenzene,
  - 1,4-Bisacetoacetylamino-2,5-dimethoxybenzene,
  - 1,4-Bisacetoacetylamino-2-bromobenzene,
  - 1,4-Bisacetoacetylamino-2,5-dibromobenzene
  - 35 1,4-Bisacetoacetylamino-2-ethylbenzene,
  - 1,4-Bisacetoacetylamino-2-ethoxybenzene,
  - 1,4-Bisacetoacetylamino-2-methoxy-5-methylbenzene,

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1,4-Bisacetoacetyl-amino-2-chloro-5-methylbenzene and  
1,4-Bisacetoacetyl-amino-2-chloro-5-methoxybenzene.

The diazotization and coupling may also be carried  
5 out in the presence of suitable organic solvents,  
such as glacial acetic acid, lower alkanols, dioxan,  
formamide, dimethyl formamide, dimethyl sulfoxide,  
pyridine or N-methyl-pyrrolidone. In order to obtain the  
full tinctorial strength, it is often advantageous to  
10 heat the coupling mixture for some time, for example by  
boiling it or maintaining it under pressure at temperatu-  
res of more than 100°C, optionally in the presence of  
organic solvents, such as lower alkanols, for example  
ethanol or isobutanol, halogenated aromatic hydrocarbons,  
15 such as chlorobenzene or dichlorobenzenes, e.g. o-dichlo-  
robenzene; dimethyl formamide, N-methyl pyrrolidone or  
in the presence of resin soap. Particularly pure pigments  
of high tinctorial strength are obtained with the  
products of the invention, if after coupling the moist  
20 press cakes or the dried powders are subjected to a  
thermal aftertreatment with organic solvents, such as  
alcohols, above all lower alkanols, pyridine, glacial  
acetic acid, dimethyl formamide, N-methyl pyrrolidone,  
dimethyl sulfoxide, halogenated aromatic hydrocarbons  
25 such as chlorobenzene or dichlorobenzenes, for example  
o-dichlorobenzene, or nitrobenzene, or if the pigments  
are subsequently ground with the addition of grinding  
auxiliaries.

30 The term "lower" relating to alkyl radicals includes  
groups of from 1 to 6, especially 1 to 4, carbon atoms.

The pigments may also be prepared in the presence of  
a carrier material, for example baryte.

35

The novel compounds are water-insoluble and insoluble  
in the common organic solvents and are suitable for

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pigmenting printing inks, varnished and dispersion paints, for dyeing caoutchouc, plastics and natural or synthetic resins.

- 5 They are further appropriate for the pigment printing on substrates, especially textile fiber materials or other flat articles, such as paper.

10 The pigments may also be used for other fields of application, for example in a finely divided form of the dyeing of rayon or viscose or cellulose ethers or esters, polyamides, polyurethanes, polyglycol terephthalates or polyacrylonitriles in the spinning mass, or for the dyeing of paper.

- 15 The pigments have a high tinctorial strength and can easily be processed in the mediums mentioned above. The dyeings have a very good fastness to light and weather and are resistant to the influence of chemicals, especially to solvents.
- 20

The following Examples illustrate the invention, the percentages relating to the weight. Temperatures are given in °C.

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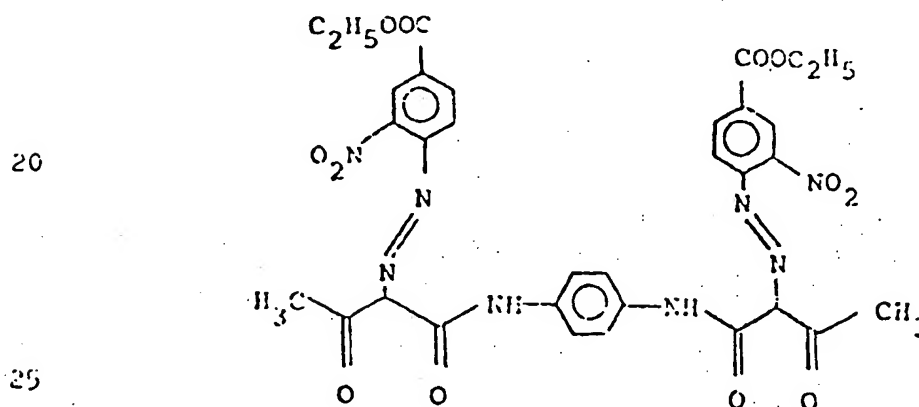
Example 1

- 10.5 grams of 3-nitro-4-aminobenzoic acid ethyl ester are stirred for 1 hour at 10°C in a mixture of 80 ml of  
30 glacial acetic acid and 15 ml of 31 % hydrochloric acid. Thereafter 10 ml of 5N sodium nitrite solution are rapidly added dropwise, and stirring is continued for 30 minutes (Disazo solution). 7.3 g of 1,4-bisaceto-acetylamino-benzene are suspended in 200 ml of water and dissolved  
35 with 5 ml of 33 % sodium hydroxide solution. For coupling the above-mentioned disazo solution is introduced into a stirring vessel and mixed with 200 ml of ice water

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- and 10 ml of a 10 % aqueous solution of oleyl alcohol which has been reacted with 30 mols of ethylene oxide. Within one hour the alkaline solution of the 1,4-bis-aceto-acetylamino-benzene is added dropwise, while
- 5 maintaining the pH at about 3 - 4, with a 5 % aqueous solution of sodium acetate. After finishing the coupling stirring is continued for 30 minutes, the product is suction-filtered and washed with water until salt-free.
- 10 The press cake is suspended in 800 ml of dimethyl formamide and after heating to 130°, it is maintained at this temperature for 10 minutes. The pigment is suction-filtered again, washed with dimethyl formamide, methanol and water and dried. Yield: 17.2 g of an
- 15 intensely reddish yellow pigment of the formula



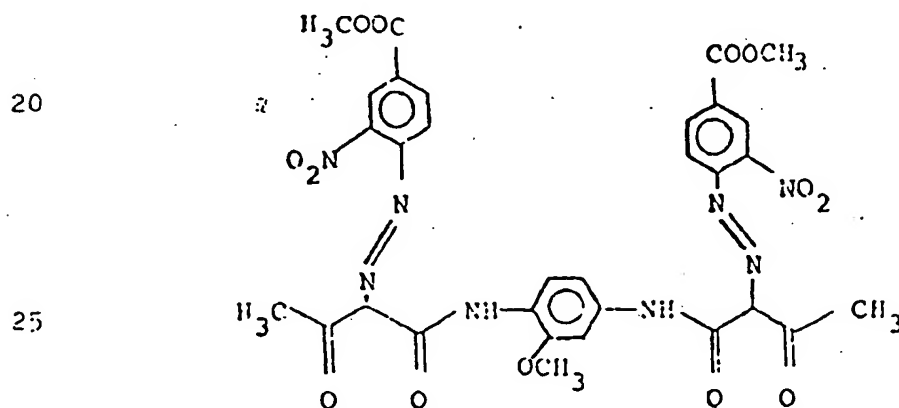
### Example 2

- 19.6 g of 3-nitro-4-aminobenzoic acid methyl ester are
- 30 stirred in a mixture of 160 ml of glacial acetic acid and 30 ml of 30 % hydrochloric acid. The reaction mixture is cooled to 10° and under the surface of this mixture there is rapidly introduced a solution of
- 35 20 ml of 5 N-sodium nitrite (diazotizing agent.)

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16 g of 1,4-bisaceto-acetyl-amino-2-methoxy-benzene are dissolved in a mixture of 300 ml of water and 10 ml of 33 % sodium hydroxide solution (coupling component). For coupling there are first introduced into a stirring vessel 300 ml of ice water, 30 ml of 2 N-sodium acetate solution, 6 ml of glacial acetic acid and 20 ml of a 10 % aqueous solution of oleyl alcohol which has been reacted with 30 mols of ethylene oxide. At 10° the solutions of the diazo and the coupling component flow within one hour simultaneously to the buffer mixture. After coupling, the product is heated for 30 minutes to 80° and suction-filtered. The pigment is dried at 70°, heated for a short time to 110° in 400 ml of N-methylpyrrolidone, suction-filtered, washed with methanol and water and dried. 34.8 g of reddish-yellow pigment with high tinctorial strength of the formula



are obtained.

30 The following table gives further Examples of disazo compounds which are obtained by coupling the diazotized aromatic amines (diazo component) of the formula II with the coupling components of the formula III:

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Example	Formula II		Formula III		tint
	No.	R	X	Y	
5	3	CH <sub>3</sub>	H	H	reddish-yellow
	4	CH <sub>3</sub>	Cl	H	"
	5	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	H	orange
10	6	CH <sub>3</sub>	CH <sub>3</sub>	H	reddish-yellow
	7	CH <sub>3</sub>	Cl	Cl	yellow
	8	CH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	yellowish-brown
15	9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	orange
	10	C <sub>2</sub> H <sub>5</sub>	Cl	H	reddish-yellow
	11	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	H	yellowish-orange
20	12	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	H	orange
	13	C <sub>2</sub> H <sub>5</sub>	Cl	Cl	greenish-yellow
	14	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	yellowish-orange
25	15	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	yellowish-brown
	16	C <sub>2</sub> H <sub>5</sub>	Br	H	reddish-yellow
	17	CH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>	orange
30	18	n-C <sub>3</sub> H <sub>7</sub>	H	H	reddish-yellow
	19	n-C <sub>4</sub> H <sub>9</sub>	H	H	"



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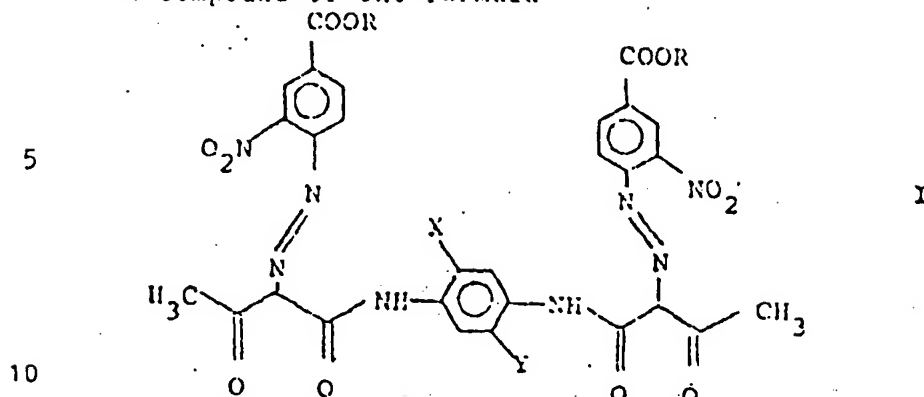
Example No.	Formula II R	Formula III		tint
		X	Y	
20	CH <sub>3</sub>	Cl	OCH <sub>3</sub>	yellowish- orange
21	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	reddish- yellow
22	C <sub>2</sub> H <sub>5</sub>	Cl	CH <sub>3</sub>	yellow

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I claim:

1. A compound of the formula



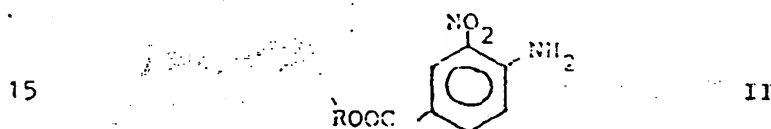
wherein R is alkyl of 1 to 4 carbon atoms and X and Y are hydrogen, chlorine, bromine, methyl, ethyl, methoxy or ethoxy.

- 15 2. A compound as claimed in Claim 1, wherein R is methyl or ethyl.
3. A compound as claimed in Claim 1, wherein X and Y are hydrogen, chlorine, methyl or methoxy.
- 20 4. The compound as claimed in Claim 1, wherein R is ethyl and X and Y are hydrogen.
5. The compound as claimed in Claim 1, wherein R is methyl, X is methoxy and Y is hydrogen.
- 25 6. The compound as claimed in Claim 1, wherein R is methyl and X and Y are hydrogen.
- 30 7. The compound as claimed in Claim 1, wherein R is methyl and X and Y are chlorine.

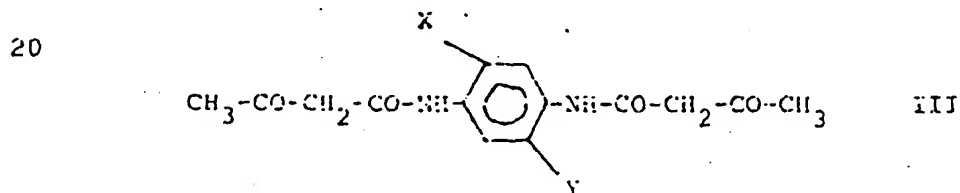
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8. The compound as claimed in Claim 1, wherein R, X and Y are methyl.
9. The compound as claimed in Claim 1, wherein R is ethyl and X and Y are methyl.
10. The compound as claimed in Claim 1, wherein R is ethyl and X and Y are chlorine.
11. A process for the preparation of a compound as claimed in Claim 1 which comprises diazotizing two molar equivalents of a compound of the formula II



and coupling onto a compound of the formula III



- 25 wherein R, X and Y are as defined in Claim 1.
12. A process as claimed in Claim 11, wherein a mixture of amines of formula II are diazotized.
13. A process as claimed in Claims 11 and 12, wherein the diazotized amine or mixture of amines is coupled onto a mixture of compounds of formula III.
14. A process for pigmenting articles which comprises incorporating into said article a compound as claimed in Claim 1.

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icles which comprises  
layer containing a

1.

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15. A process for pigmenting  
coating said article with  
compound as claimed in C